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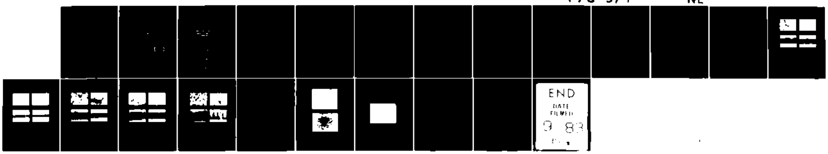

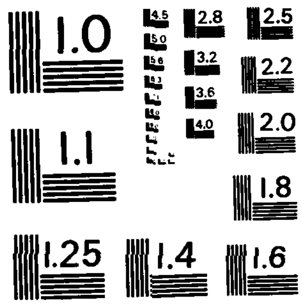


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FINAL REPORT

by
L. YANG



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Contract No. N00014-81-C-2633



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GA PROJECT 3781
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# CHEMICAL VAPOR DEPOSITION OF ORIENTED TUNGSTEN FOILS FOR THERMIONIC CATHODES

## INTRODUCTION

This report summarizes the work carried out under Contract N00014-81-C-2633 during the period of October 1, 1981 to November 30, 1982. The objective of this work is to prepare tungsten thermionic emitters containing preferred crystallographic orientations by chemical vapor deposition techniques for the improvement of the performance of dispenser cathodes.

For the past several years, a new type of dispenser cathode has been under development under the sponsorship of the Naval Research Laboratory (NRL).(1) In contrast to the conventional dispenser cathode which employs pressed and sintered tungsten powder matrix impregnated with Ba/BaO as the electron emitter, this new type of dispenser cathode uses for the emitting surface a thin tungsten foil (~25 micron thickness) containing a controlled array of small holes (e.g., 5 micron diameter and 15 micron distance between the centers of adjacent holes) for regulating the dispensation and vaporization loss of Ba/BaO from a reservoir behind the foil. This new type of dispenser cathode is called the Controlled Porosity Dispenser (CPD) cathode.

Chemical vapor deposition (CVD) techniques are specially suited for the fabrication of CPD cathodes for two reasons. First, the emitting surface and the supporting structure of the cathode can be prepared as an integral unit without any welded or brazed joints. Secondly, CVD tungsten prepared under special conditions can have certain crystallographic planes oriented preferentially parallel to the geometric surface (2),(3),(4),(5). Such oriented emitters may help to improve the uniformity and magnitude of electron emission from CPD cathodes, since it has been observed that the thermionic emission from Ba/BaO covered surfaces is dependent upon the crystal orientation of the metal substrate(6),(7).

Efforts under the present contract were devoted to the preparation of CVD tungsten emitters containing a variety of preferred crystallographic orientations. The work is divided into two phases.

In Phase I, a CVD tungsten deposition apparatus was built and CVD tungsten samples of various preferred crystallographic orientations were prepared and characterized with respect to microstructures and nature and degree of preferred orientations. These samples were delivered to NRL for the evaluation of their electron emission properties.

In Phase II, efforts were made to produce a high degree of preferred crystallographic orientations in thin CVD tungsten deposits (~25 micron thickness) which are amenable to hole drilling by laser. Techniques for preparing CVD tungsten cathode structure were established and samples of oriented tungsten cathode structure were prepared for NRL evaluation.

The details of the work are described in this report.

PHASE I WORK

1. Assembly of CVD Tungsten Deposition Apparatus

Tungsten can be chemical vapor deposited by hydrogen reduction of tungsten hexafluoride or tungsten chloride. The deposits are called fluoride tungsten and chloride tungsten, respectively. By controlling the deposition conditions, fluoride tungsten and chloride tungsten of various preferred orientations can be obtained.

A CVD apparatus capable of accommodating both fluoride and chloride tungsten deposition was built to provide a variety of preferred orientations. Figure 1 and Figure 2 show the arrangements for fluoride tungsten and chloride tungsten deposition, respectively. In both cases, the molybdenum mandrel on which the tungsten is deposited is heated by induction, and the flow rates of the gaseous reactants are measured by mass flowmeters (for tungsten hexafluoride and chlorine) or sapphire-ball flowmeters (for hydrogen). The major differences are: (1) the tungsten hexafluoride is introduced into the deposition chambers as a gas from a gas cylinder, while the tungsten chloride is formed at the top of the deposition chamber by the chlorination of CVD tungsten chips, (2) the gas pressure in the deposition chamber for fluoride tungsten deposition is much higher than that for chloride tungsten deposition (~250 torrs versus 10 torrs), (3) the mandrel is rotated at the rate of 1 RPM during chloride tungsten deposition in order to improve the uniformity of the deposit, while the mandrel remains stationary during fluoride tungsten deposition since the higher pressure in the deposition chamber helps to distribute the deposit uniformly and therefore rotation of the mandrel is not necessary, and (4) the temperature of the mandrel is measured with a Chromel-Alumel thermocouple during fluoride tungsten deposition, and with a micro-optical pyrometer during chloride tungsten depositon. The other components shown in Figure 1 and Figure 2 are self-explanatory.

2. Preparation of Oriented CVD Tungsten Samples for NRL Evaluation

CVD tungsten samples of five different preferred crystallographic orientations were prepared for NRL evaluation. The deposition conditions are shown in Table 1. Each molybdenum mandrel with the tungsten on it was cut into two halves with a diamond impregnated cutting disc. The surface of one-half was ground smooth with an Alundum wheel, polished with "0000" emery paper, and electropolished in 10% NaOH. The surface of the other half was left in the as-deposited state. Discs of about 3.6 mm diameter were obtained from each half by electrical-discharge-machining. The oriented tungsten samples were recovered from these discs after the molybdenum mandrel was removed by dissolution in a mixture of equal volumes of water, concentrated $HNO_3$ and concentrated $H_2SO_4$. These samples were then outgassed in vacuum at 1200°C for 2 hours. The nature of the preferred orientation and the distribution of the preferred orientation crystallographic axes of the outgassed samples were determined with a

Norelco pole figure machine. Their thicknesses were measured with a digital micrometer. Remnants from the two halves of the deposit were examined for their surface morphology by scanning electron microscopy and their bulk microstructures by optical metallography. Table 2 summarizes the characteristics of these samples. Figure 3 through Figure 7 show their surface morphology, bulk microstructures and the distributions of the preferred orientation axes. These samples were delivered to NRL for the evaluation of their electron emission properties.

## PHASE II WORK

1. Establishment of Deposition Conditions for Obtaining (100) Preferred Orientation in thin (~25 micron thickness) Fluoride Tungsten Deposits.

Since successful laser-drilling can be accomplished only if the tungsten emitting layer is 25 microns or less in thickness, it is therefore necessary to find out whether a high degree of preferred orientation can be obtained in such thin deposits.

Preliminary results obtained by NRL on the samples shown in Table 2 indicate that the (100) oriented sample has the potential for electron emission improvement.[8] Efforts were therefore made to define the conditions under which a high degree of (100) preferred orientation can be obtained in fluoride tungsten deposits of about 25 micron thickness. It was observed that in the temperature range 400-500°C and for hydrogen flow rates of 1000 to 2000cc/minute and $H_2/WF_6$ ratios of 5 to 20, fluoride tungsten deposits of 25 micron thickness can be obtained with 90% of the <100> axes falling within ±10° from the surface normal. Thus it appears that the (100) oriented tungsten deposit which has the potential for electron emission improvement, is also the one which can achieve a high degree of preferred orientation in thin deposits over a wide range of deposition conditions.

2. Preparation of Oriented CVD Tungsten Cathode Structures.

Techniques were developed for the preparation of oriented CVD tungsten cathode structures, with the emitting surface either in the as-deposited state or in the electropolished state. The steps involved are shown in Figure 8.

Two (100) oriented fluoride tungsten cathode structures were prepared according to these techniques. Cathode structure No. 1 has an electropolished emitting surface. Cathode structure No. 2 has an as-deposited emitting surface. Both have an emitting surface of 25 micron thickness and a cylindrical supporting structure of 3.56mm I.D., 125 micron thickness, and 9.52mm height. Figure 9 shows the surface morphology of these cathode structures. Figure 10 shows the typical microstructures of such thin (100) oriented fluoride tungsten emitting layers. Figure 11 shows the distributions of the <100> axes in the emitting layers of these two cathode structures, which were obtained by tilting the sample manually on a Norelco pole figure

machine and reading the diffraction intensity at various tilting angles. Such manual operation is necessary since the automatic tilting mechanism also causes the sample to oscillate. With a sample of only 3.6mm in diameter, the oscillation motion leaves the sample out of the X-ray beam for a significant part of the exposure time. The moving mechanism of the machine is now being modified in order to allow automatic sample tilting in the future. Both cathode structures were delivered to NRL for the evaluation of their electron emission property.

## CONCLUSION

The work described above has shown that CVD tungsten can be deposited in a variety of preferred crystallographic orientations and that a high degree of (100) preferred orientations can exist even in a very thin (~25 microns) layer of CVD tungsten deposits. In addition, CVD techniques have been developed for preparing cathode structures free of welded and brazed joints. Thus the work accomplished under the present contract has demonstrated the potential of chemical vapor deposited tungsten for improving the performance and simplifying the fabrication procedures of dispenser cathodes.

Further work should include the development of techniques for producing a controlled array of holes on such oriented CVD tungsten emitters, such as laser-drilling, and chemical and electrochemical etching, using masks made by photolithographic techniques. This should be followed by the evaluation of the performance of such oriented CPD tungsten cathodes in established test vehicles.

Table 1. Deposition Conditions for CVD Tungsten Samples of Various Preferred Orientations

| Sample Desig-nation | Type of CVD Tungsten | Mandrel Temp. ($^oC$) | Flow Rate (cc/min.) $H_2$ | Flow Rate (cc/min.) $WF_6$ | Flow Rate (cc/min.) $Cl_2$ | Tungsten Chip Temp. ($^oC$) | Chamber Pressure (torr) | Deposition Time (hour) | Deposit Thickness (Micron) | Preferred Orien-tation |
|---|---|---|---|---|---|---|---|---|---|---|
| 8509-9 | Fluoride | 500 | 2000 | 350 | - | - | 250 | 1/2 | 180 | (100) |
| 8509-13 | Fluoride | 500 | 2000 | 25 | - | - | 250 | 1 | 68 | (411) |
| 8509-25 | Chloride | 1350 | 350 | - | 115 | 850 | 10 | 1 | 185 | (211) |
| 8509-29 | Chloride | 1250 | 250 | - | 115 | 850 | 10 | 1 | 263 | (111) |
| 8509-59 | Chloride | 1100 | 140 | - | 115 | 850 | 10 | 1 | 320 | (110) |

Table 2. Characteristics of CVD Oriented Tungsten Samples Delivered to NRL

| Sample Designation | Sample No. | Preferred Orientation | Surface Finish | Diameter (mm) | Thickness (Micron) |
|---|---|---|---|---|---|
| 8509-9 | 1 | (100) | As-deposited | 3.61 | 180 |
| | 2 | | Electropolished | 3.61 | 133 |
| 8509-13 | 3 | (411) | As-deposited | 3.58 | 68 |
| | 4 | | Electropolished | 3.58 | 63 |
| 8509-25 | 5 | (211) | As-deposited | 3.61 | 185 |
| | 6 | | Electropolished | 3.61 | 155 |
| 8509-29 | 7 | (111) | As-deposited | 3.58 | 263 |
| | 8 | | Electropolished | 3.61 | 195 |
| 8509-59 | 9 | (110) | As-deposited | 3.66 | 320 |
| | 10 | | Electropolished | 3.66 | 228 |

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(8) Private communication from R. E. Thomas of Naval Research Laboratory.

June 7, 1983

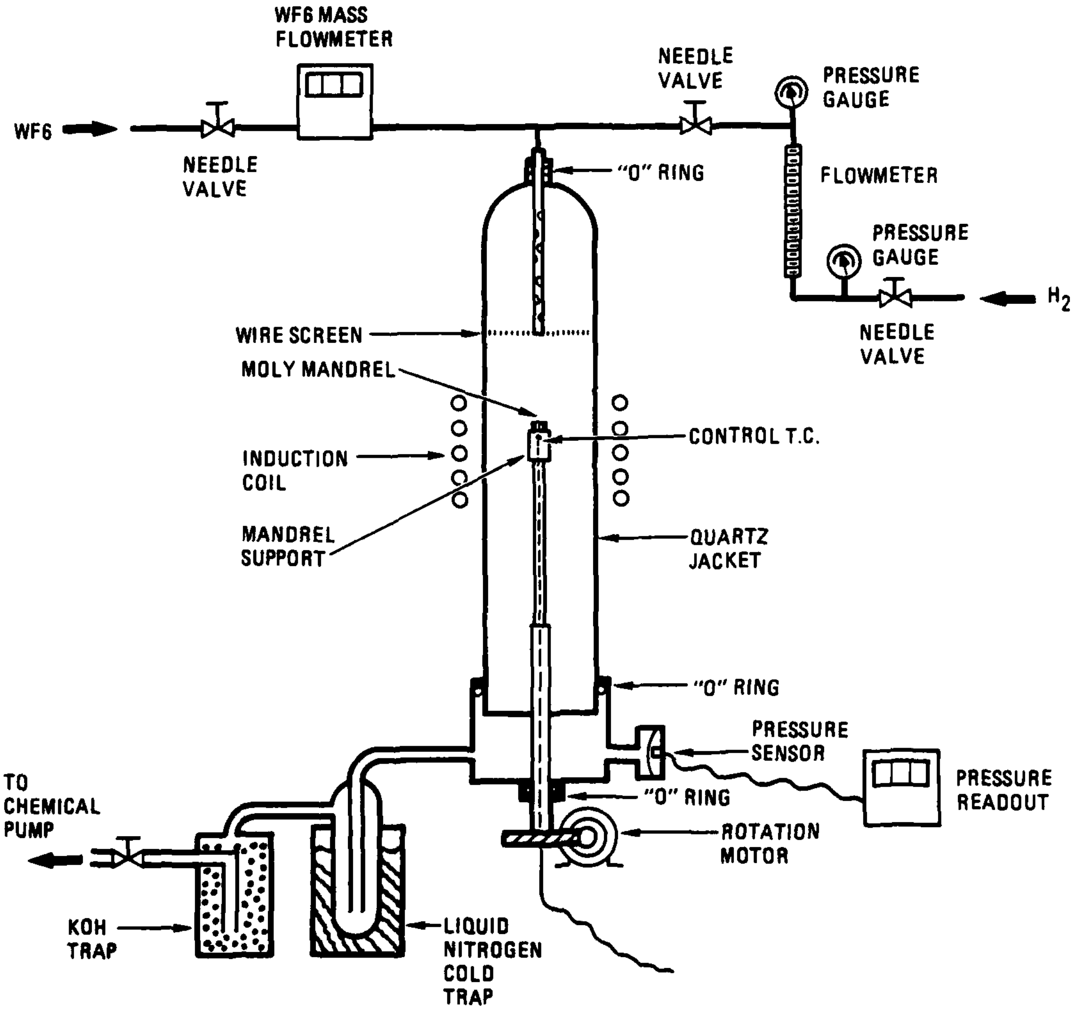



Figure 1. Arrangement for Chemical Vapor Depos
by Hydrogen Reduction of Tungsten He.

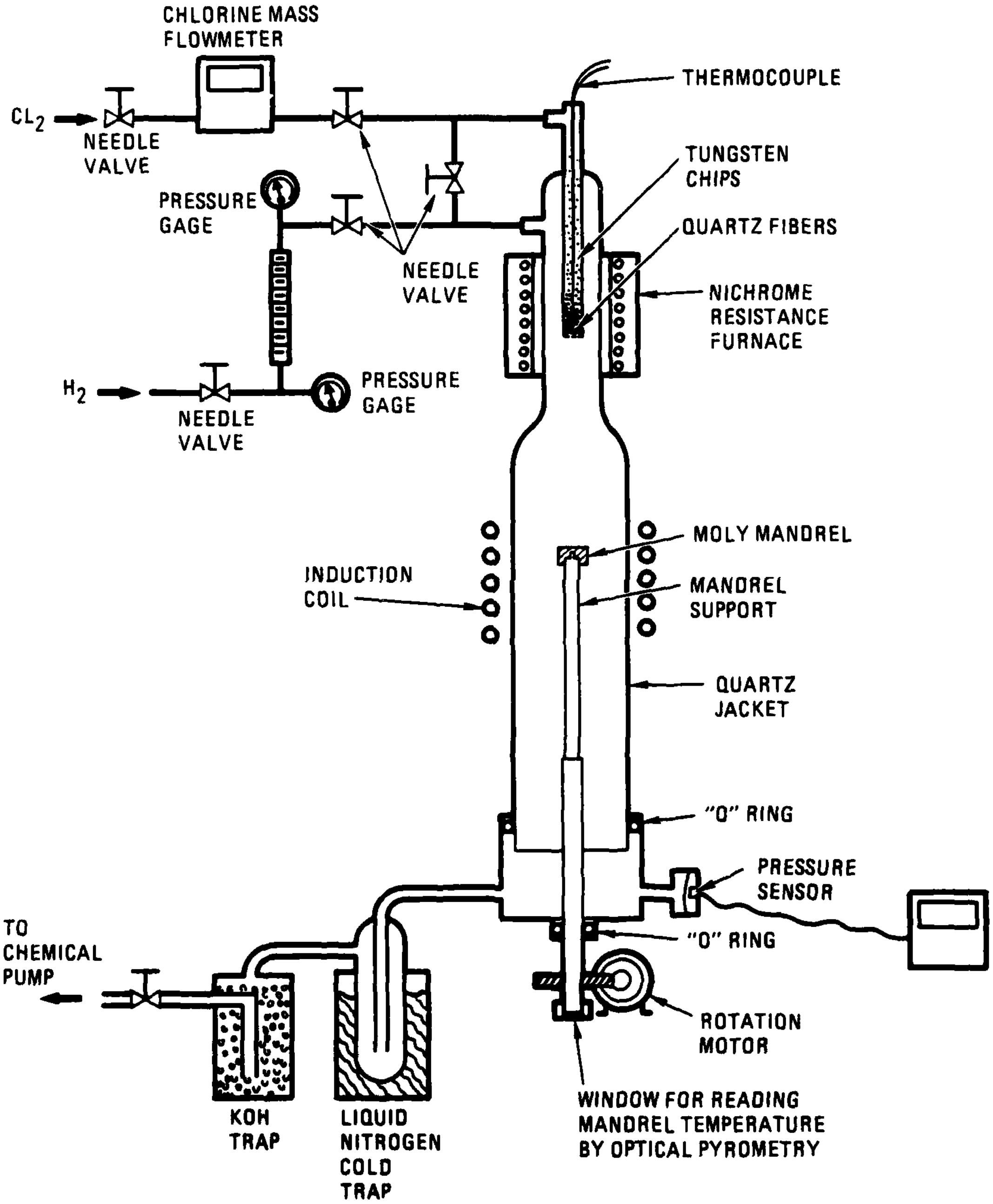



Figure 2. Arrangement for Chemical Vapor Deposition of Tungsten by Hydrogen Reduction of Tungsten Chloride.

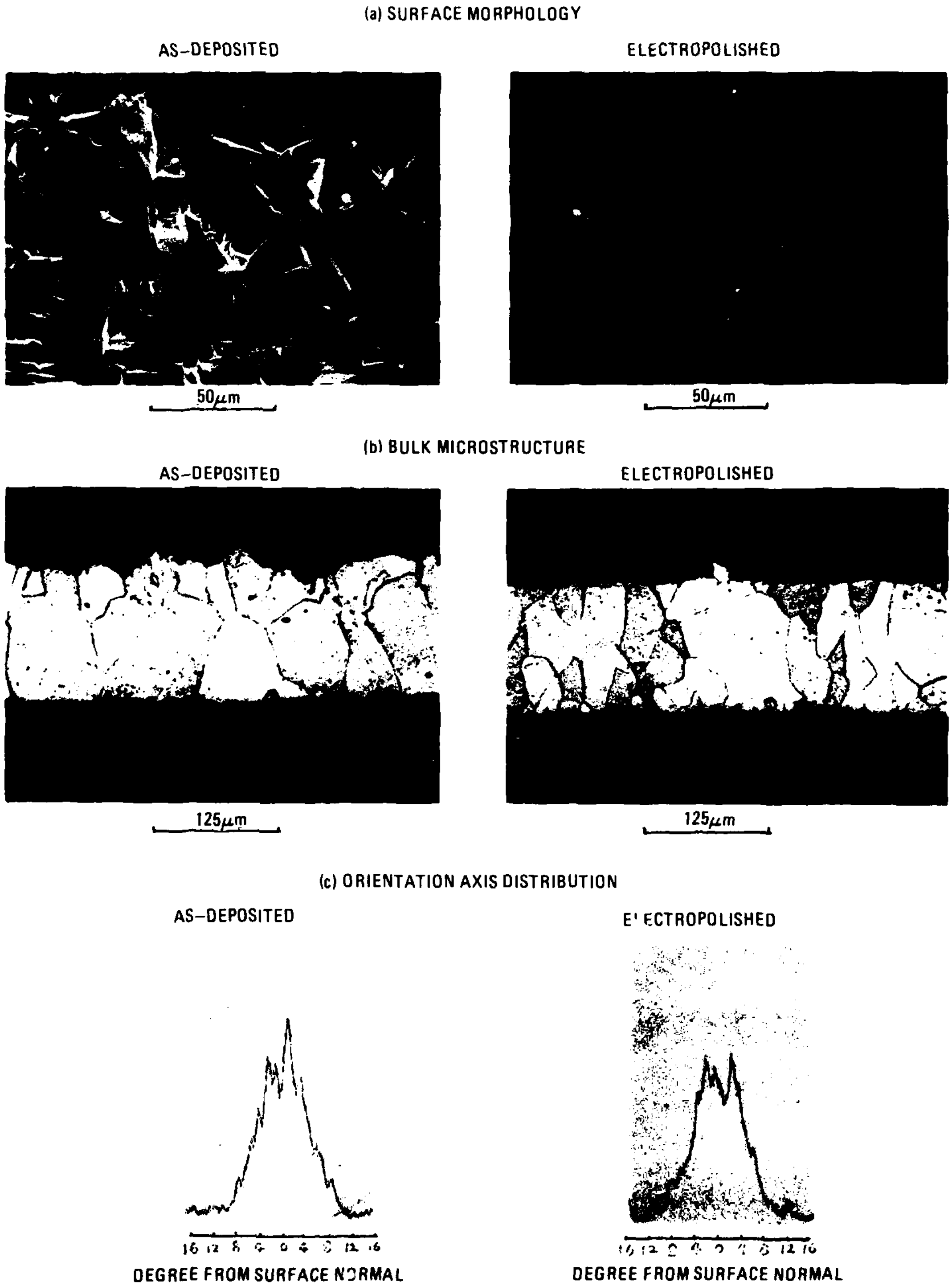



Figure 3. (100) Oriented Tungsten Sample

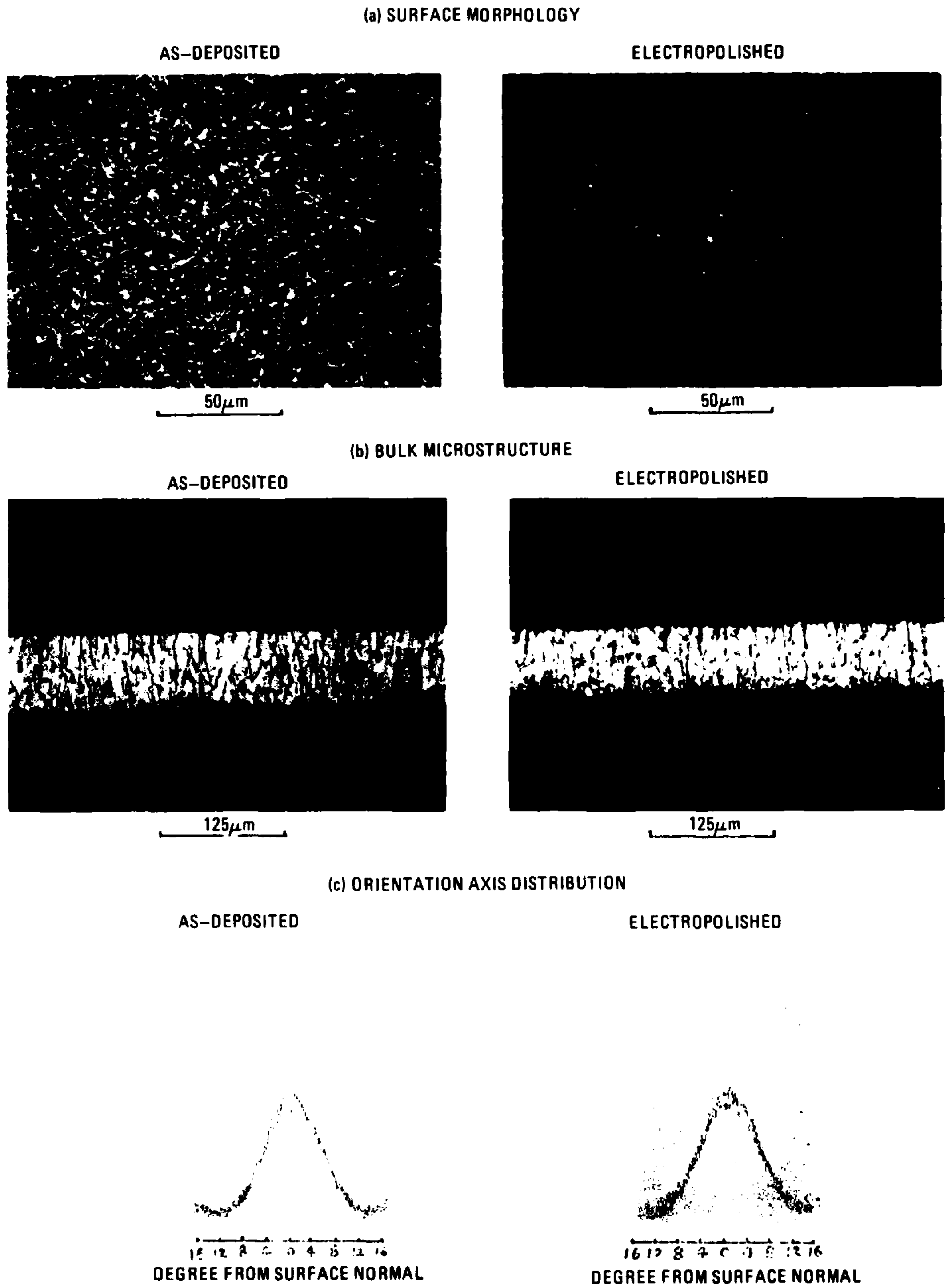



Figure 4. (411) Oriented Tungsten Sample

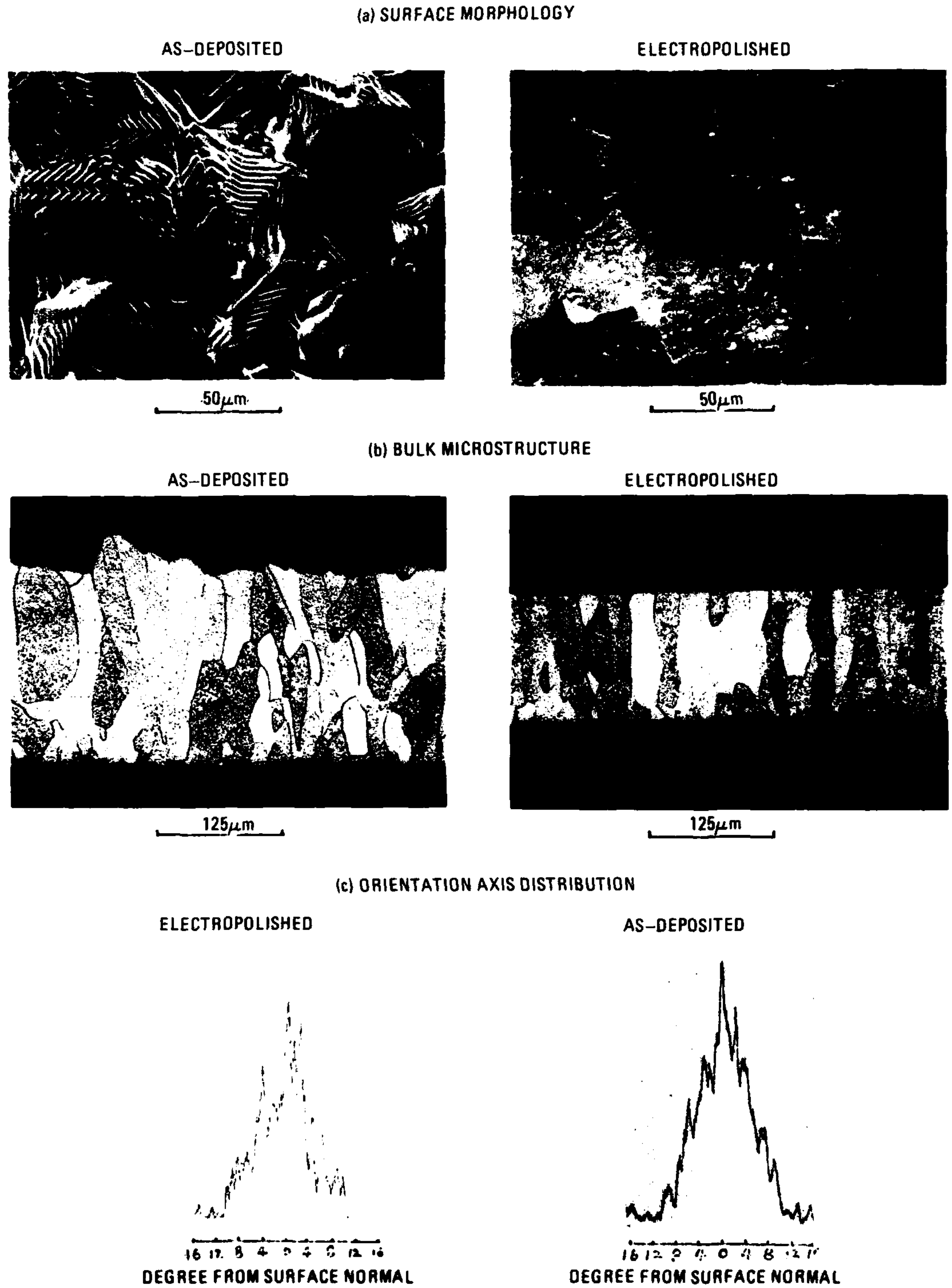



Figure 5. (211) Oriented Tungsten Sample

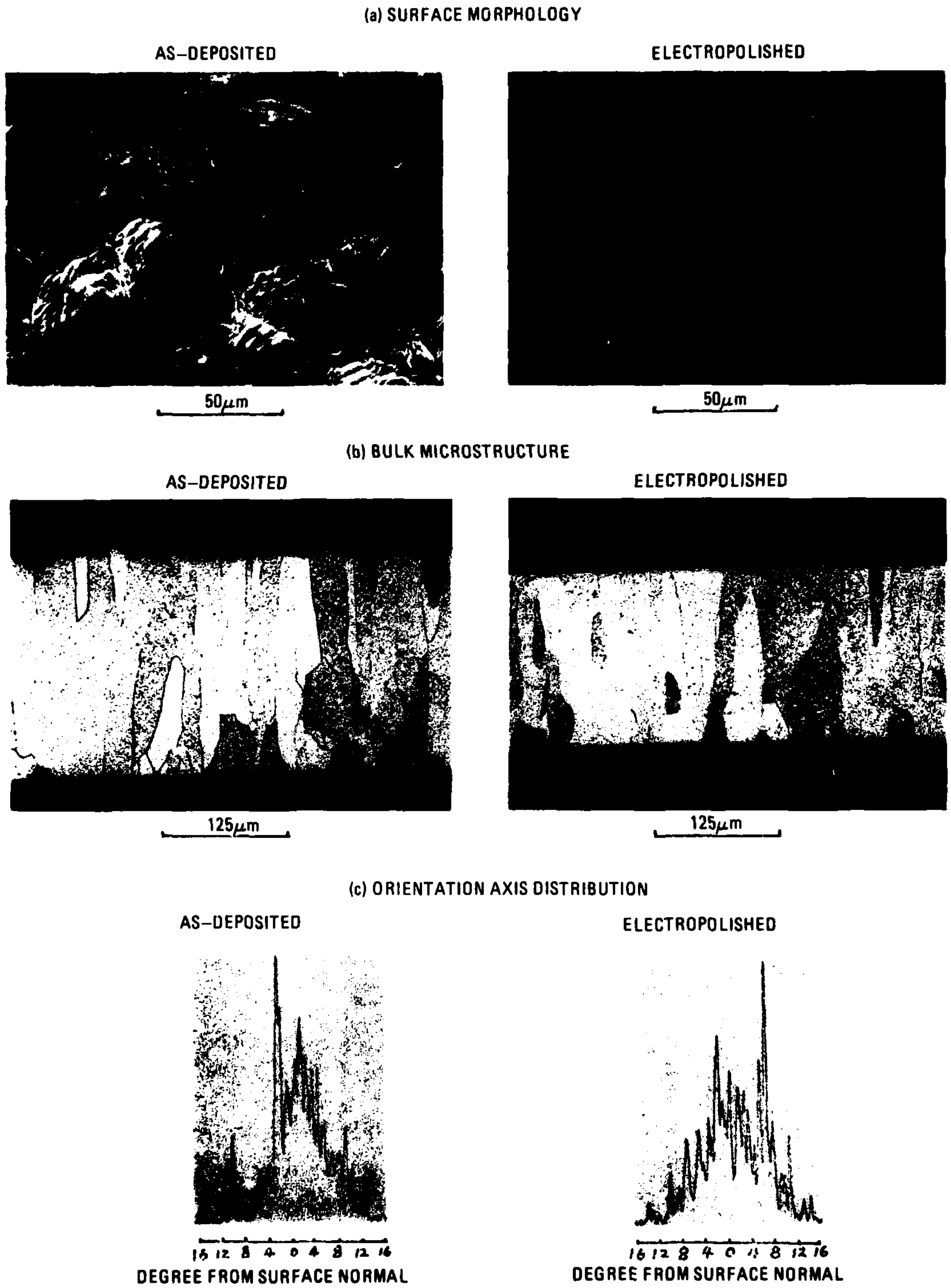



Figure 6. (111) Oriented Tungsten Sample

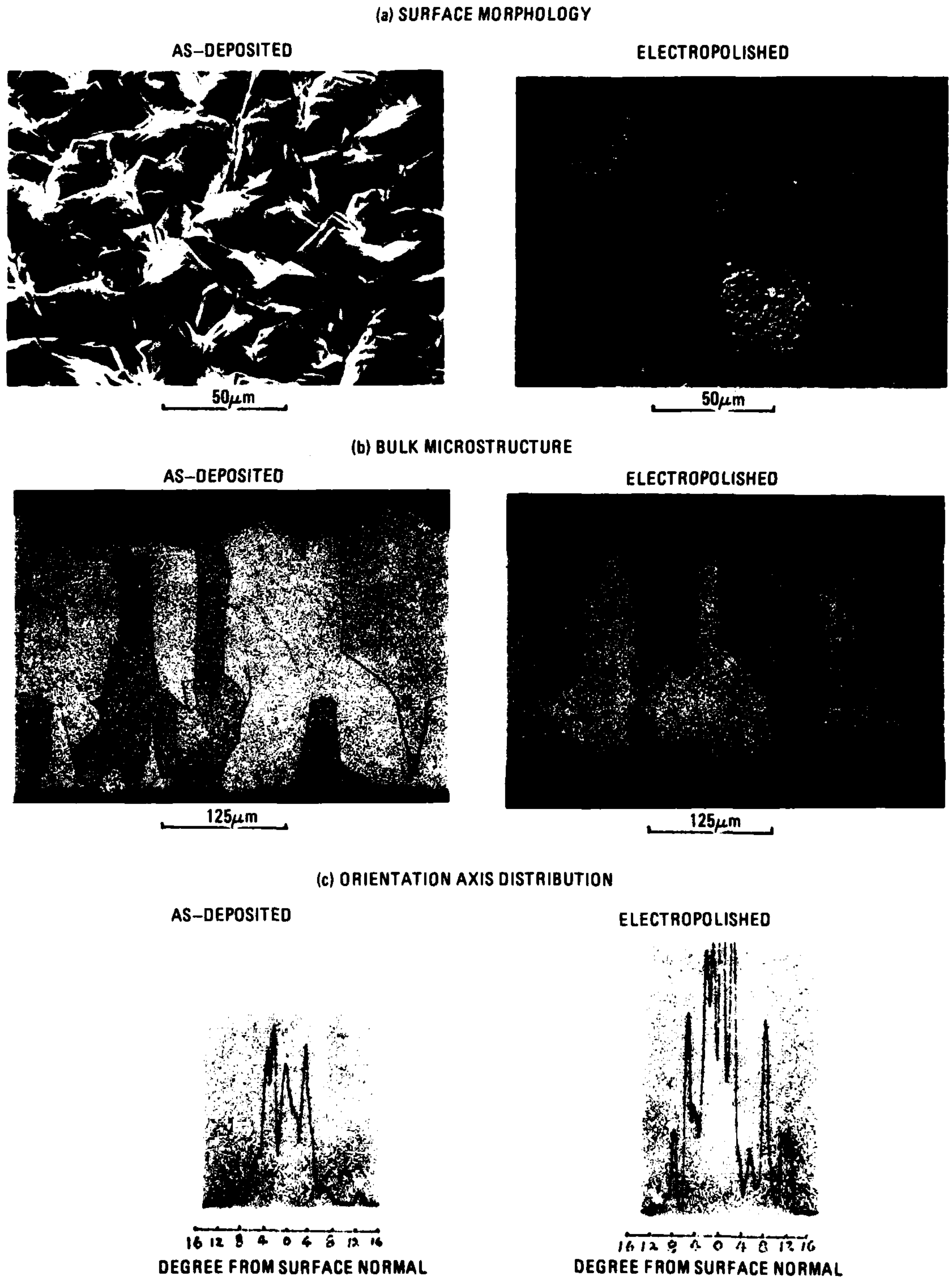



Figure 7. (110) Oriented Tungsten Sample

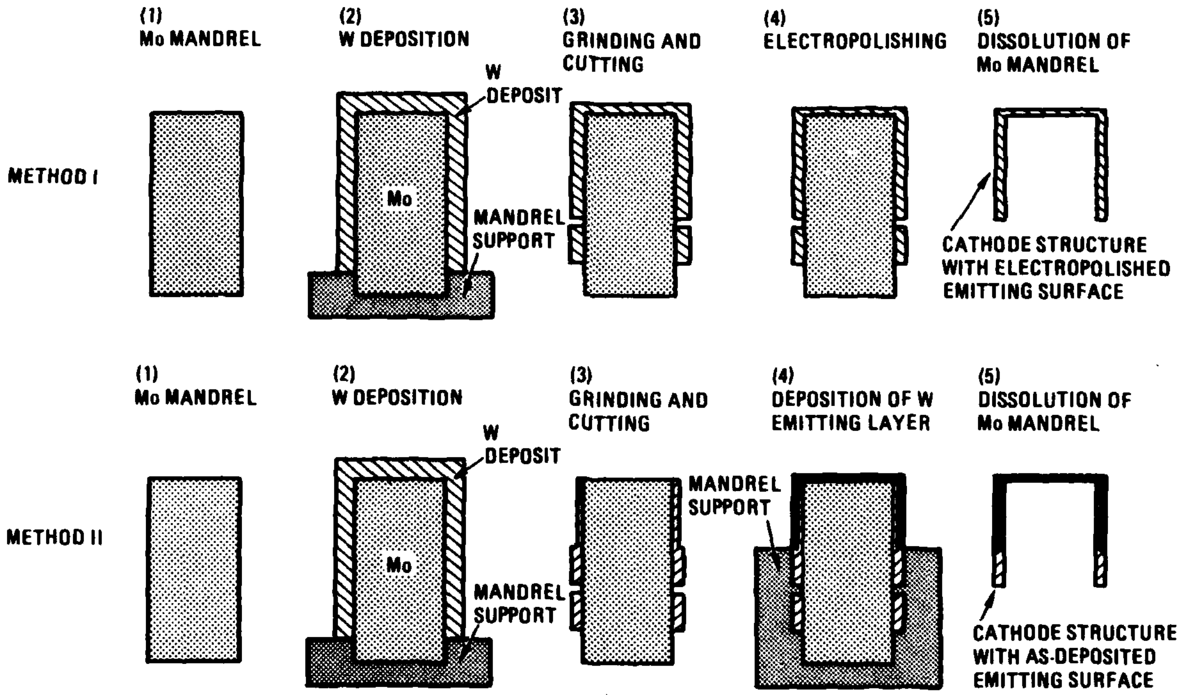
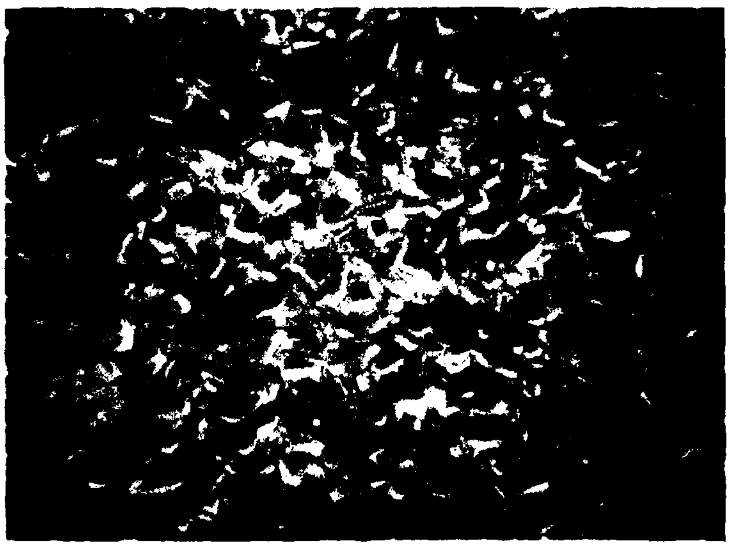



Figure 8. PREPARATION OF CVD TUNGSTEN CATHODE STRUCTURE

(a) ELECTROPOLISHED

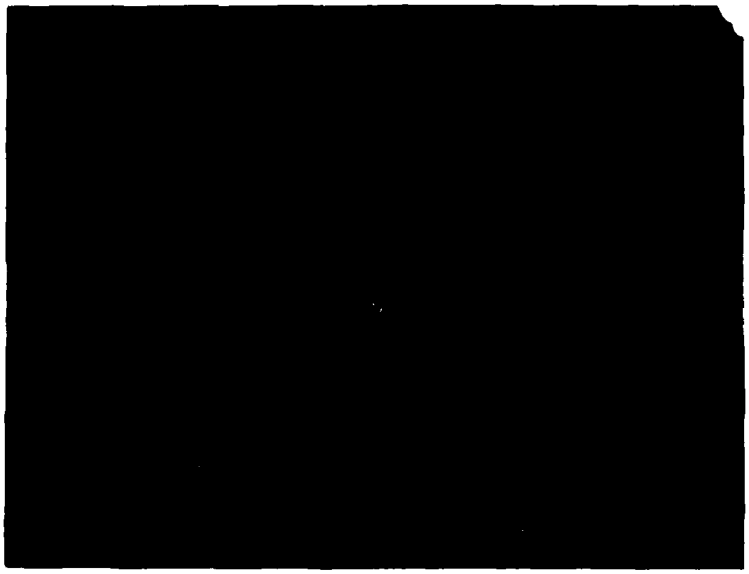
40μm



(b) AS–DEPOSITED

40μm

Figure 9. Surface Morphology of the Emitting Surface of (100) Oriented Tungsten Cathode Structures



$80 \mu m$

Figure 10. Typical Microstructures of a Cross Section of the Emitting Layer of (100) Oriented Tungsten Cathode Structures

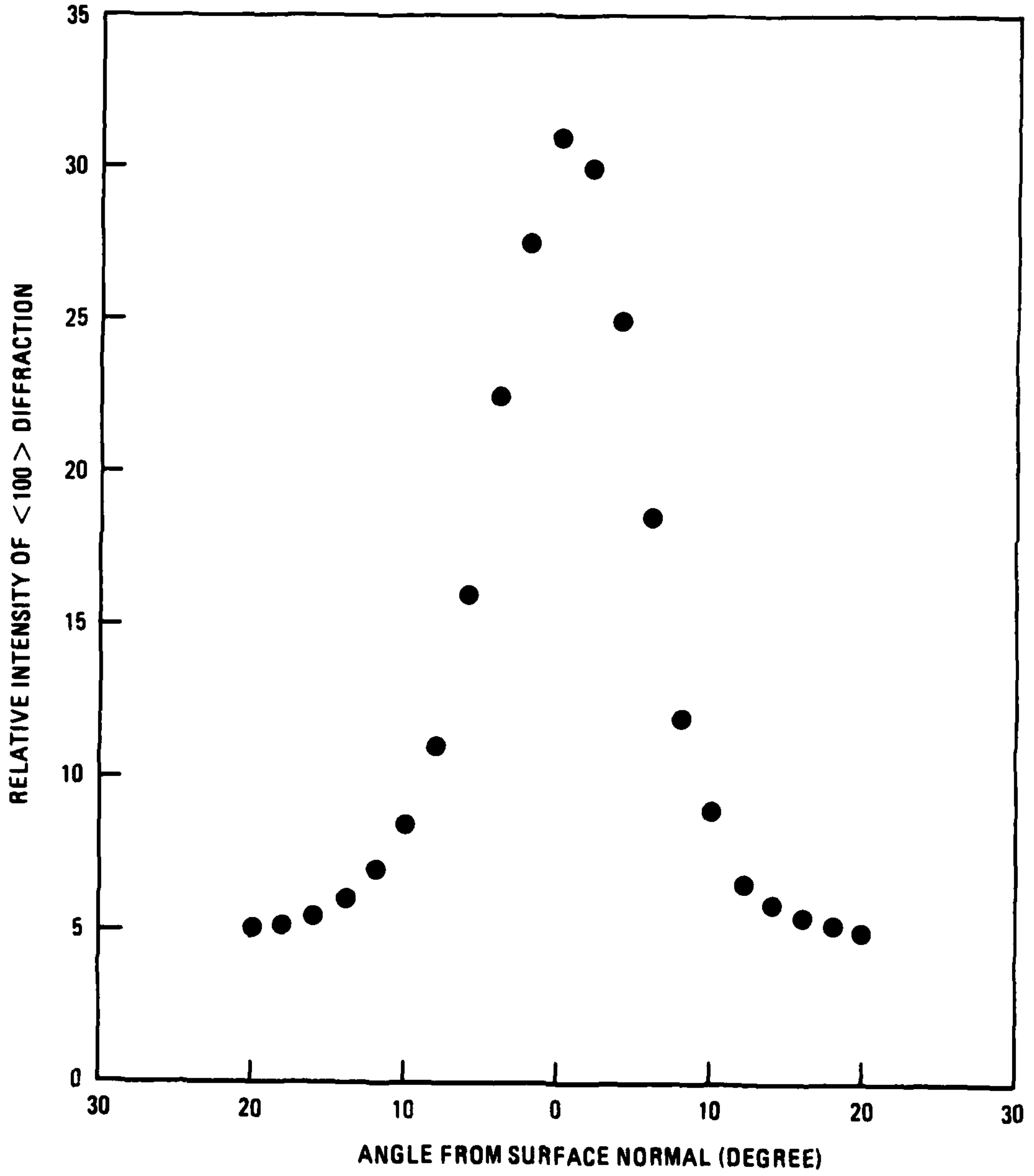



Figure 11(a). Distribution of <100> Orientation in Electropolished Cathode Structure No. 1.

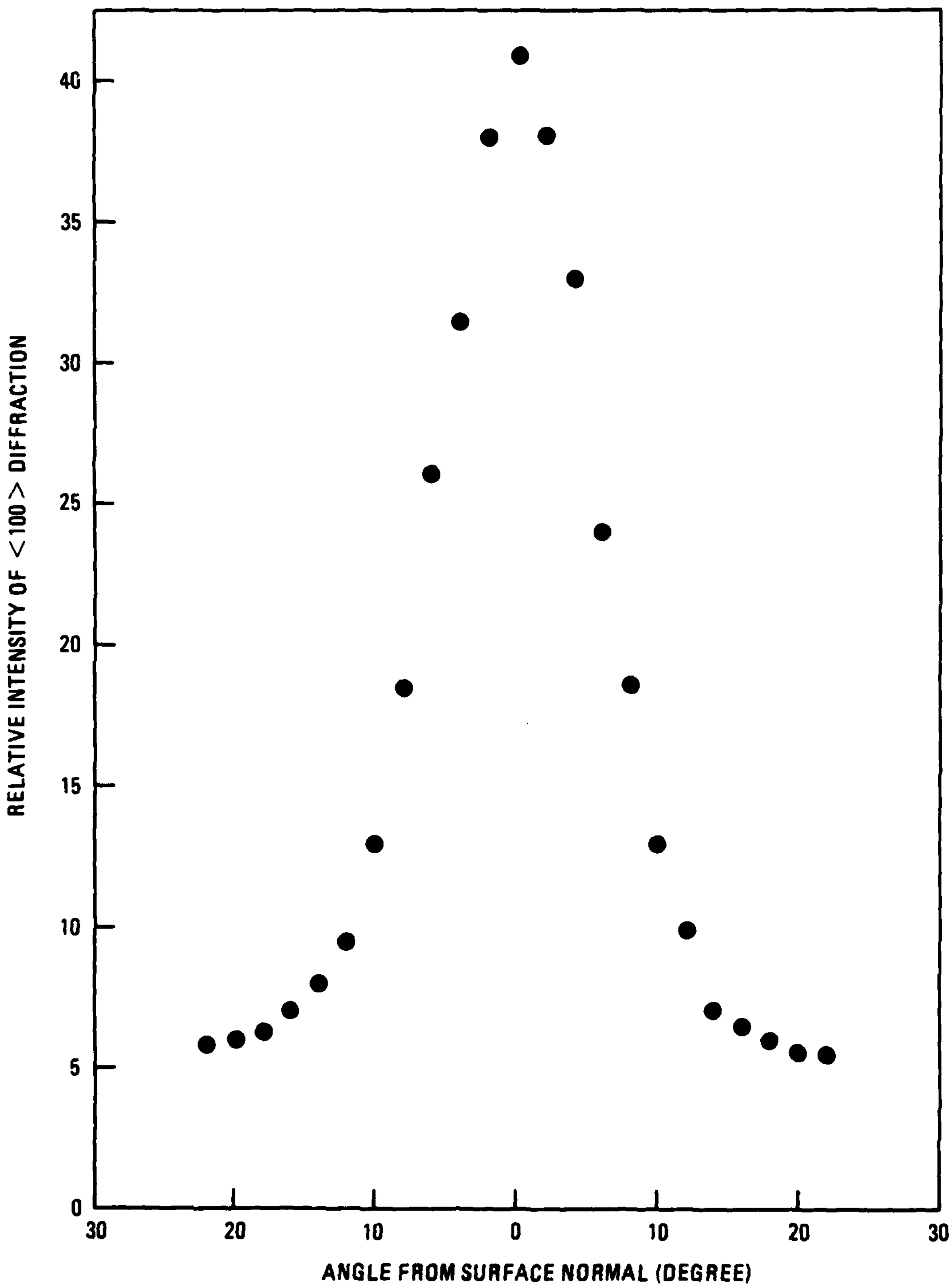



Figure 11(b). Distribution of <100> Orientation in As-Deposited Cathode Structure No. 2.

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